

Anticipated Classification  
of this Application:  
Class 430 Subclass \_\_\_\_\_

03-17-00  
Prior Application:  
Examiner Christopher RoDee  
Group Art Unit 1753

Attorney's A  
Docket  
No. 54490-Z/JPW/DVD

03/16/00  
Jc699 U.S. PTO  
09/526602  
03/16/00  
PATENTABLE ASSISTANT COMMISSIONER FOR PATENTS  
Washington, D.C. 20231

March 16, 2000

PTO:

This is a request for filing a \_\_\_\_\_ CONTINUATION

☒ DIVISIONAL \_\_\_\_\_ CONTINUATION-IN-PART application under

☒ 37 C.F.R. §1.53(b) \_\_\_\_\_ 37 C.F.R. §1.53(d), of pending prior application  
Serial No. 08/911,616 filed on August 15, 1997 of

Yasuharu Suda and Hiroaki Kuno for  
Inventor(s)

LIQUID TONER COMPOSITION AND METHOD OF MANUFACTURING THE SAME  
Title of Invention

1. ☒ Enclosed is a copy of the prior application, as originally  
filed and an affidavit or declaration verifying it as a  
true copy.
2. \_\_\_\_\_ A verified statement to establish small entity status under  
37 C.F.R. §1.9 and 1.27  
\_\_\_\_\_ is enclosed.  
\_\_\_\_\_ was filed in the prior application and such status  
is still proper and desired (37 C.F.R. §1.28(a)).
3. ☒ The filing fee is calculated as follows:

CLAIMS AS FILED, LESS ANY CLAIMS CANCELLED BY AMENDMENT

	NUMBER FILED		NUMBER EXTRA*		RATE		FEE	
					SMALL ENTITY	OTHER ENTITY	SMALL ENTITY	OTHER ENTITY
Total Claims	7-20	=	0	X	9	18	= \$	\$ 0
Independent Claims	1-3	=	0	X	39	78	= \$	\$ 0
Multiple Dependent Claims Presented: _____ Yes <input checked="" type="checkbox"/> No					130	260	= \$	\$ 0
*If the difference in Col. 1 is less than zero, enter "0" in Col. 2.					BASIC FEE		\$ 345.00	\$690.00
					TOTAL FEE		\$	\$690.00

<sup>1</sup> filing an application pursuant to this section expressly abandons the  
parent application.

4. X The Commissioner is hereby authorized to charge payment of the following fees associated with this application or credit any overpayment to Deposit Account No. 03-3125.
- X Any additional filing fees required under 37 C.F.R. §1.16.
- X Any patent application processing fees under 37 C.F.R. §1.17.
- The issue fees set forth in 37 C.F.R. §1.18 at or before mailing of the Notice of Allowance, pursuant to 37 C.F.R. §1.311(b).
5. X Three copies of this sheet are enclosed.
6. X A check in the amount of \$ 690.00 is enclosed.
7.        Cancel claims       .
8.        Amend the specification by inserting before the first line the sentence: --This is a        continuation X divisional of application Serial No. 08/911,616, filed August 15, 1997--
9. X 1 Sheet(s) of        informal X formal drawing(s) is/are enclosed.
10.        Transfer the drawings from the prior application to this application and abandon said prior application as of the filing date accorded this application. A duplicate copy of this sheet is enclosed for filing in the prior application file.
11. X Priority of application No. 8-215765 filed on August 15, 1996 in Japan (country) is claimed under 37 U.S.C. §119.
- X The certified copy of the priority application has been filed in prior application Serial No. 08/911,616, filed August 15, 1997.
12. X The prior application is assigned of record to Mitsubishi Heavy Industries, LTD..
13. X A preliminary amendment is enclosed.
14. X The power of attorney in the prior application is to:

And I hereby appoint John P. White (Reg. No. 28,678), Thomas F. Moran (Reg. No. 16,579), Norman H. Zivin (Reg. No. 25,385), Ivan S. Kavrukov (Reg. No. 25,161), Christopher C. Dunham (Reg. No. 22,031), Thomas G. Carulli (Reg. No. 30,616), Robert D. Katz (Reg. No. 30,141), Peter J. Phillips (Reg. No. 29,691), Richard S. Milner (Reg. No. 33,970), Matthew J. Golden (Reg. No. 35,161), Albert Wai-Kit Chan (Reg. No. 36,479) and Lewis Kreisler (Reg. No. 38,522), each of whose address is 1185 Avenue of the Americas, New York, N.Y. 10036, or any one of them, my attorneys with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, and request that correspondence be directed to Cooper & Dunham LLP, 1185 Avenue of the Americas, New York, N.Y., 10036

- (a)   X   The power appears in the original papers in the prior application.
- (b)        Since the power does not appear in the original papers, a copy of the power in the prior application is enclosed.
- (c)   X   Address all future communications to:  
(May only be completed by applicant,  
or attorney or agent of record.)

John P. White

Cooper & Dunham LLP

1185 Avenue of the Americas

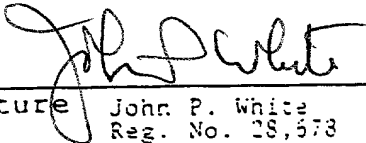
New York, New York 10036

15.   X   Also enclosed Express Mail Certificate of Mailing bearing  
Express Mail Label No. EM525891341US dated March 16, 2000, Information  
Disclosure Statement with Form PTO-1449 (Exhibit 1) and a copy of  
a European Search Report (Exhibit 2)

16.   X   I hereby verify that the attached papers are a true copy  
of prior application Serial No. 08/911.616 as originally  
filed on August 15, 1997

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statement and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

March 16, 2000  
Date

  
Signature John P. White  
Reg. No. 28,573

       INVENTOR(S)  
       ASSIGNEE OF COMPLETE INTEREST  
  X   ATTORNEY OR AGENT OF RECORD  
       FILED UNDER 37 C.F.R. §1.34(a)

Address of Signator:

Cooper & Dunham LLP

1185 Avenue of the Americas

New York, New York 10036

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants : Yasuharu Suda and Hiroaki Kuno  
U.S. Serial No. : Not Yet Known  
Filed : Herewith  
For : LIQUID TONER COMPOSITION AND METHOD OF  
MANUFACTURING THE SAME

1185 Avenue of the Americas  
New York, New York 10036  
March 16, 2000

Assistant Commissioner for Patents  
Washington, D.C. 20231

Box: Patent Application

Sir:

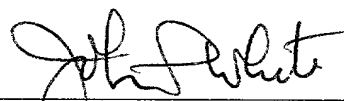
**EXPRESS MAIL  
CERTIFICATE OF MAILING  
FOR ABOVE-IDENTIFIED APPLICATION**

"Express Mail" Mailing Label Number: EM 525 891 341 US  
Date of deposit: March 16, 2000

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. §1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231

  
Printed Name Jamel Rhabb

Respectfully submitted,

  
John P. White  
Registration No. 28,678  
Attorney for Applicant(s)  
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1185 Avenue of the Americas  
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Dkt. 54490-Z/JPW/DVD

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants : Yasuharu Suda and Hiroaki Kuno  
U.S. Serial No. : Not Yet Known  
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MANUFACTURING THE SAME

1185 Avenue of the Americas  
New York, New York 10036  
March 16, 2000

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

PRELIMINARY AMENDMENT

Please amend the subject application as follows.

In the Specification:

On page 1, line 5, please insert the following as a separate paragraph:

--This application is a divisional of U.S. Serial No. 08/911,616, filed August 15, 1997, which claimed priority of Japanese Patent No. 8-215765, filed August 15, 1996.--

In the Claims:

Please cancel claims 1-13 without prejudice to applicants' right to pursue the subject matter of these claims in a future application.

Applicants: Yasuharu Suda and Hiroaki Kuno  
Serial No.: Not Yet Known  
Filed: Herewith  
Page 2

Please add new claims 14-20 as follows:

- 14. (New) A method of manufacturing a liquid toner composition for electrophotography, comprising the steps of:

heating a thermoplastic resin within a solvent capable of dissolving said thermoplastic resin when heated and substantially incapable of dissolving said resin at room temperature, the SP (solubility parameter) value of said solvent being adjusted to control the particle diameter of toner particles based on a difference between the SP value of the resin itself and the SP value of the solvent, to melt and mix the resin with the solvent; and cooling the mixture to permit precipitation of the toner particles, wherein inorganic fine particles are added to the mixture immediately before initiation of the toner particle precipitation so as to permit the toner particle precipitation.--

- 15. (New) The method of manufacturing a liquid toner composition for electrophotography according to claim 1, wherein said inorganic fine particles consist of silica particles or silica particles to which a hydrophobic treatment is applied.--

- 16. (New) The method of manufacturing a liquid toner composition for electrophotography according to claim 1, wherein said inorganic fine particles consist of titanium oxide particles or titanium hydroxide particles.--

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- 17. (New) The method of manufacturing a liquid toner composition for electrophotography according to claim 1, wherein the surfaces of the inorganic fine particles are treated with an organic material or a hydroxide.--
- 18. (New) The method of manufacturing a liquid toner composition for electrophotography according to claim 1, wherein said liquid toner composition further contains at least one of a charge controller and a dispersant.--
- 19. (New) The method of manufacturing a liquid toner composition for electrophotography according to claim 5, wherein said charge controller is added in an amount of 0.5 to 50% by weight based on the solid components of the liquid toner composition.--
- 20. (New) The method of manufacturing a liquid toner composition for electrophotography according to claim 5, wherein said dispersant is added in an amount of 0.5 to 80% by weight based on the solid components of the liquid toner composition.--

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Serial No.: Not Yet Known  
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REMARKS

By this Amendment, applicants have amended the specification to recite the continuing data for the above-identified application. Accordingly, applicants maintain that the amendment to the specification raises no issue of new matter and respectfully request that this amendment be entered.

Claims 1-13 were pending in the subject application. By this Amendment applicants have canceled claims 1-13 and added new claims 14-20. Accordingly, upon entry of this Amendment, claims 14-20 will be pending and under examination. New claims 14-20 correspond to the subject matter of Group II of the claims identified by the Examiner in a restriction requirement issued August 3, 1998 in connection with U.S. Serial No. 08/911,616 which is the parent of the subject application.

Applicants maintain that new claims 14-20 raise no issue of new matter and that these claims are fully supported by the specification as filed.

Support for new claim 14 may be found inter alia in the specification, as originally-filed, at page 3, lines 12-23. Support for new claims 15 and 16 may be found inter alia in the specification, as originally-filed, at page 4, lines 21-24; and page 8, lines 16-20.

Support for new claim 17 may be found inter alia in the specification, as originally-filed, at page 8, line 27 through page 9, line 4. Support for new claim 18 may be found inter alia in the specification, as originally-filed, at page 9, lines 22-24.



Applicants: Yasuharu Suda and Hiroaki Kuno  
Serial No.: Not Yet Known  
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Page 5

Support for new claim 19 may be found inter alia in the specification, as originally-filed, at page 10, line 17-22. Support for new claim 20 may be found inter alia in the specification, as originally-filed, at page 11, line 11-15.

Accordingly, applicants respectfully request that the Amendment be added.

#### INFORMATION DISCLOSURE STATEMENT

In accordance with their duty of disclosure under 37 C.F.R. §1.56, applicants would like to direct the Examiner's attention to the following references which are listed on the attached Form PTO-1449 (**Exhibit 1**). These references were previously cited in connection with the prosecution of U.S. Serial No. 08/911,616, from which the subject application claims benefit under 35 U.S.C. §120. According to 37 C.F.R. §1.98(d), copies of patents or publications that were previously cited by, or submitted to, the Office in connection with such prior applications need not accompany the Information Disclosure Statement. Accordingly, copies of the following references are not attached to this Information Disclosure Statement:

1. U.S. Patent No. 4,058,470 to Moschovis et al., issued November 15, 1977;
2. U.S. Patent No. 3,939,087 to Vijayendran et al., issued February 17, 1976;
3. European Patent Application Publication No. 0 224 912 to Larson James, R., published June 10, 1987;

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4. Obata Shinichiro, Patent Abstracts of Japan, vol.95, no. 11, August 15, 1995;
5. Higuchi Yoichi, Patent Abstracts of Japan, vol. 18, no. 48, October 22, 1993;
6. Yamamoto Kyoichi, Patent Abstracts of Japan, vol. 17, no. 485, May 18, 1993; and
7. DATABASE WPI Abstract of Publication No. JP 53 057 039 dated May 24, 1978.

Applicants maintain that none of the above-listed references discloses or suggests applicant's claimed invention.

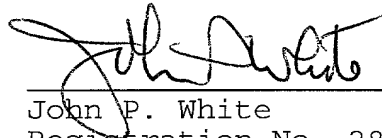
Applicants also submit herewith as **Exhibit 2**, a copy of a European Search Report issued November 28, 1997 in connection with corresponding European Patent Application No. EP 97 11 3883.9.

If a telephone interview would be of assistance in advancing the prosecution of the subject application, applicants' undersigned attorney invites the Examiner to telephone the number provided.

Applicants: Yasuharu Suda and Hiroaki Kuno  
Serial No.: Not Yet Known  
Filed: Herewith  
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No fee, other than the enclosed fee of \$690.00 for filing the subject application, is deemed necessary in connection with the filing of this Preliminary Amendment. However, if any additional fee is required, authorization is hereby given to charge the amount of such fee to Deposit Account No. 03-3125.

Respectfully submitted,



---

John P. White  
Registration No. 28,678  
Attorney for Applicants  
Cooper & Dunham LLP  
1185 Avenue of the Americas  
New York, New York 10036  
(212) 278-0400

**Application  
for  
United States Letters Patent**

**To all whom it may concern:**

*Be it known that We,  
Yasuharu Suda and Hiroaki Kuno  
have invented certain new and useful improvements in*

**LIQUID TONER COMPOSITION AND METHOD OF MANUFACTURING THE SAME**

*of which the following is a full, clear and exact description.*

# TITLE OF THE INVENTION

LIQUID TONER COMPOSITION AND METHOD OF MANUFACTURING  
THE SAME

## BACKGROUND OF THE INVENTION

5           The present invention relates to a liquid toner composition and a method of manufacturing the same.

          The conventional liquid toner composition for electrophotography comprises, for example, an electrically insulating carrier liquid, coloring  
10           particles dispersed in the carrier liquid, a resin soluble in an electrically insulating liquid and serving to disperse and fix the coloring particles, and a charge controller for charging the coloring materials positive or negative. The coloring particles contained  
15           in the composition are excellent in dispersion capability to make the toner composition excellent in resolution. However, the conventional liquid toner composition is poor in its fixing capability. Also, the agglomerating force of the coloring particles is  
20           low in the image portion. It follows that, when a picture image is transferred from a photosensitive body to a supporting sheet, the image is likely to be collapsed so as to bring about flow of the toner particles, leading to deterioration of the transferred  
25           picture image.

          As a measure for overcoming the above-noted difficulty, proposed is a liquid toner composition

prepared by dispersing toner particles consisting of a pigment and a resin in an electrically insulating liquid, said resin being substantially insoluble in said electrically insulating liquid. Also proposed in, for example, Japanese Patent Publication (Kokoku) No. 5-87825, is a technical idea that the toner particles are shaped to have fiber-like projections so as to increase the agglomerating force among the toner particles.

However, if the agglomerating force among the toner particles dispersed in a liquid is unduly high, the toner particles tend to be excessively agglomerated to form large coarse particles which are likely to be precipitated. Further, in the step of developing the electrostatic latent image formed on the surface of a photosensitive body, the presence of the agglomerated toner particles brings about reduction of resolution.

#### BRIEF SUMMARY OF THE INVENTION

An object of the present invention is to provide a liquid toner composition containing toner particles which do not exhibit a high agglomerating force and are excellent in dispersion capability during storage and development of the composition, and which exhibit an increased agglomerating force in the transferring step so as to suppress collapsing and flow of the picture image, leading to an improved picture image. The present invention is also intended to provide a method

of manufacturing the particular liquid toner composition.

According to a first aspect of the present invention, there is provided a liquid toner composition  
5 prepared by dispersing toner particles consisting essentially of a colorant and a resin in a carrier liquid, the resultant composition forming an electrorheological fluid.

The property of forming an electrorheological  
10 fluid is herein called ER (Electro Rheological) property.

According to a second aspect of the present invention, there is provided a method of manufacturing a liquid toner composition, comprising the step of  
15 heating, dissolving, mixing and dispersing a thermoplastic resin in a solvent having a high temperature dependency in its capability of dissolving the thermoplastic resin and having its solubility parameter adjusted for controlling the size of toner  
20 particles, followed by cooling to permit the toner particles to be precipitated, wherein inorganic fine particles are added by at latest the stage immediately before initiation of the toner particle precipitation.

Additional object and advantages of the invention  
25 will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The object and

advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

5       BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

          The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate presently preferred embodiments of the invention, and together with the general description  
10       given above and the detailed description of the preferred embodiments given below, serve to explain the principles of the invention.

          Figure shows how to evaluate the ER property of the liquid toner composition of the present invention.

15       DETAILED DESCRIPTION OF THE INVENTION

          The present invention provides a liquid toner composition prepared by dispersing toner particles consisting essentially of a colorant and a resin in a liquid carrier. It is desirable for inorganic fine  
20       particles to be attached to or impregnated in at least the surface region of the toner particle. The inorganic fine particles used in the present invention are formed of, for example, silica, silica which is made hydrophobic, titanium oxide or titanium hydroxide.

25       A pigment used in general for preparing an ink composition, a toner composition, etc. can be used in the present invention as the colorant contained in the



liquid toner composition. For example, a black pigment used in the present invention includes various carbon blacks including all the carbon blacks prepared by, for example, a furnace method, a contact method and an acetylene method and available on the market for use in the manufacture of rubber and a coloring material and for use as an electrically conductive material. To be more specific, classification of carbon black is given on pages 290 to 291 of "Carbon Black Binran (Manual)" published in April, 1995. The carbon black used in the present invention includes any classification of HCF, MCF, RCF, LCF, LFF, which are prepared by a furnace method, and HCC, MCC, RCC, LCC, which are prepared by a channel method. Further, various acetylene blacks given on page 294 of "Carbon Black Binran" noted above can also be used in the present invention.

The non-black pigment used in the present invention as the colorant includes, for example, phthalocyanine blue, phthalocyanine green, sky blue, rhodamine lake, malachite green lake, Hansa yellow, benzidine yellow, and brilliant carmine 6B.

The pigment can be used in combination with a dye such as an oil soluble azo dye including oil black and oil red, a basic azo dye including bismark brown, an acidic azo dye including blue black HF, and quinone imine dye including nigrosine. Further, it is possible to use a so-called "processed pigment", i.e., a pigment

having the surface coated with a resin.

The colorant is added in advance to a thermoplastic resin by means of kneading under heat.

Alternatively, the colorant can be added during  
5 manufacture of the liquid toner composition of the present invention. Specifically, the colorant can be added before precipitation of the toner particles.

The resin used in the present invention should desirably a thermoplastic resin including, for example,  
10 vinyl chloride resin, vinylidene chloride resin, vinyl acetate resin, polyvinyl acetal resin, styrene series resin, methacrylic acid series resin, polyethylene resin, polypropylene resin, fluorine-containing resin, polyamide series resin, polyacetal resin, and saturated  
15 polyester resin. It is particularly desirable to use olefin resins having carboxyl groups or ester bonds including, for example, ethylene-vinyl acetate copolymer, partially saponified ethylene-vinyl acetate copolymer, ethylene-acrylic acid copolymer, ethylene-methacrylic acid copolymer, ethylene-acrylic acid ester  
20 copolymer, ethylene-methacrylic acid ester copolymer, acrylic acid ester resin, methacrylic acid ester resin, styrene-acrylic acid copolymer, styrene-methacrylic acid copolymer, styrene-acrylic acid ester copolymer, and styrene-methacrylic acid ester copolymer. These  
25 resins can be used singly or in the form of a mixture of at least two kinds of resins. Also, these resins

can be mixed in an amount of 50 to 99% by weight relative to 50 to 1% by weight of the pigment.

The carrier liquid used in the present invention includes, for example, a linear or branched aliphatic hydrocarbon, alicyclic hydrocarbon and halogenated derivatives thereof. It is also possible to use silicone oils. Specific examples of the carrier liquid used in the present invention include, for example, Isopar G (trade name of a carrier liquid produced by Exxon Inc.), Isopar H (trade name of a carrier liquid produced by Exxon Inc.), Isopar K (trade name of a carrier liquid produced by Exxon Inc.), Isopar L (trade name of a carrier liquid produced by Exxon Inc.), Isopar M (trade name of a carrier liquid produced by Exxon Inc.), Isopar V (trade name of a carrier liquid produced by Exxon Inc.), Shellzole 71 (trade name of a carrier liquid produced by Shell Oil Co., Ltd.), IP1620 (trade name of a carrier liquid produced by Idemitsu Petrochemical Co., Ltd.), IP2028 (trade name of a carrier liquid produced by Idemitsu Petrochemical Co., Ltd.), IP2835 (trade name of a carrier liquid produced by Idemitsu Petrochemical Co., Ltd.), cyclooctane, cyclodecane, and TSF451 series (trade name of silicone oils produced by Toshiba Silicone Inc.).

The solvent used in the present invention for dissolving the resin should be capable of dissolving the resin in the heating step and should be

substantially incapable of dissolving the resin at room temperature. In the present invention, the solvent is used for controlling the diameter of the precipitated toner particles. Therefore, the SP (Solubility

5 Parameter) value of the solvent is specified in the present invention. It should be noted that a differential SP value ( $\Delta SP$ ) between the SP value of the resin itself and that of the solvent should be as small as possible for diminishing the toner particle diameter.

10 The solvent meeting the particular requirements includes, for example, linear or branched aliphatic hydrocarbons, halogenated aliphatic hydrocarbons, aromatic hydrocarbons, aliphatic alcohols and ethers. These solvents can be used singly or in the form of a

15 mixture.

The inorganic fine particles used in the present invention include, for example, silica-based particles such as silica particles and silica gel particles and titanium-based particles such as titanium oxide

20 particles and titanium hydroxide particles. The particle diameter and the specific surface area of the inorganic fine particles, which can be chosen as desired, should desirably fall within a range of between 2 nm and 500 nm in terms of the primary

25 particle diameter and within a range of between 20 m<sup>2</sup>/g and 500 m<sup>2</sup>/g, respectively.

In order to control the dispersion capability or

affinity with the resin of the inorganic fine particles,  
it is also possible to use inorganic fine particles  
having the surface treated with an organic material or  
hydroxide. Specific surface-treated silica-based  
5 inorganic fine particles used in the present invention  
include, for example, Aerozyl series particles produced  
by Japan Aerozyl Co., Ltd. such as Aerozyl 130, Aerozyl  
200, Aerozyl 200 SV, Aerozyl 200 CF, Aerozyl 300,  
Aerozyl 300 CF, Aerozyl 380, Aerozyl R972, Aerozyl R974,  
10 Aerozyl R202, Aerozyl R805, Aerozyl R812, Aerozyl OX50,  
Aerozyl TT600, Aerozyl MOX80, Aerozyl MOX170, Aerozyl  
COK84, OSCAL-135 manufactured by Shokubai-Kasei Kogyo  
K.K., pulverized silica gels of CARIACT series  
manufactured by Fuji Silicia Chemical Inc., i.e.,  
15 CARIACT-15, CARIACT-30 and CARIACT-50. On the other  
hand, specific surface-treated titanium-based inorganic  
fine particles used in the present invention include,  
for example, STR series particles produced by Sakai  
Kagaku Kogyo K.K. such as STR-40, STR-60, STR-65,  
20 STR-80, STR-100, and C-11 produced by Ishihara Sangyo  
Kaisha Ltd.

Further, an antistat and/or a dispersant can be  
added to the liquid toner composition of the present  
invention. The antistat used in the conventional  
25 developing agent can be used in the present invention.  
For example, the antistat used in the present invention  
include nigrosine series dyes; metal soaps such as

manganese naphthenate, calcium naphthenate, zirconium  
naphthenate, cobalt naphthenate, iron naphthenate, lead  
naphthenate, nickel naphthenate, chromium naphthenate,  
zinc naphthenate, magnesium naphthenate, manganese  
5 octylate, calcium octylate, zirconium octylate, iron  
octylate, lead octylate, cobalt octylate, chromium  
octylate, zinc octylate, magnesium octylate, manganese  
dodecylate, calcium dodecylate, zirconium dodecylate,  
iron dodecylate, lead dodecylate, cobalt dodecylate,  
10 nickel dodecylate, chromium dodecylate, zinc dodecylate  
and magnesium dodecylate; alkylbenzene sulphonates  
such as calcium dodecylbenzene sulphonate, sodium  
dodecylbenzene sulphonate, barium dodecylbenzene  
sulphonate; phospholipids such as lecithin and  
15 cephalin; and organic amines such as n-decyl amine.  
These antistats can be used singly or in combination.

It suffices to use the antistat in an amount  
sufficient for obtaining an antistat effect. In  
general, the amount of the antistat should be 0.5 to  
20 50% by weight, preferably 1 to 30% by weight, based on  
the amount of the solid components of the liquid toner  
composition.

The dispersant used in the present invention  
should desirably be an anionic or nonionic surfactant  
25 having ethylene oxide added thereto as a hydrophilic  
group. When it comes to the anionic surfactant, it is  
desirable to use a phosphate ester of a higher alcohol

ethylene oxide adduct, which is classified as a phosphate ester. On the other hand, the nonionic surfactant used in the present invention includes, for example, a higher alcohol ethylene oxide adduct, alkylphenol fatty acid ester ethylene oxide adduct, 5 fatty acid ethylene oxide adduct, polyhydric alcohol fatty acid ester ethylene oxide adduct, higher alkylamine ethylene oxide adduct, fatty acid amide oxide adduct, ethylene oxide adduct of fat and oil, 10 and polypropyleneglycol ethylene oxide adduct. These surfactants can be used singly or in combination. It is desirable to add the dispersant in an amount of, generally, 0.5 to 80% by weight and, preferably, 1 to 50% by weight, based on the amount of the solid 15 components of the liquid toner composition.

In developing an electrostatic image formed on the surface of a photosensitive body in an electro-photographic system using a liquid toner composition, a good dispersion capability of the toner particles 20 permits a good resolution, leading to a high quality of the picture image developed on the photosensitive surface.

On the other hand, where the picture image (toner layer) on the photosensitive surface is transferred 25 onto a supporting sheet such as a paper sheet, it is desirable for the toner particles to exhibit a high agglomerating force so as to enable the toner layer to

have a high viscosity. It should be noted that, where the toner layer has a high viscosity, it is possible to suppress collapse of the picture image and flow of the toner particles in the transferring step, leading to an improved quality of the picture image transferred onto the supporting sheet.

The liquid toner composition of the present invention exhibits an ER property, as already pointed out. It should be noted that, in the developing step, the concentration of the solid components of the composition is low so as to permit the toner particles in the composition to exhibit a high dispersion capability. It follows that a picture image of a high quality can be formed on the photosensitive surface.

On the other hand, an electric field is applied for the transferring purpose to the picture image (toner layer) formed on the photosensitive layer after the developing step. What should be noted is that the toner layer noted above has a high concentration of the solid components. When the electric field is applied to the particular toner layer, an agglomerating force is instantly generated among the toner particles by an ER effect so as to increase the viscosity of the toner layer, with the result that it is possible to suppress collapse or deformation of the picture image in the transferring step. Incidentally, the term "ER effect" noted above denotes the effect that the agglomerating



force among the toner particles dispersed in a liquid carrier is increased by the electric field application so as to increase the apparent viscosity of the liquid composition.

5           It has been found that a liquid toner composition having an ER property can be obtained by adding the inorganic fine particles defined in the present invention in the manufacturing process of the composition. Particularly, it has been found desirable  
10       to add the inorganic fine particles in an appropriate stage falling within a period between the starting step and the step immediately before precipitation of the toner particles. It is considered reasonable to understand that the inorganic fine particles are  
15       attached to or impregnated in at least the surface region of the toner particle so as to produce the ER effect.

          As described above in detail, the present invention provides a liquid toner composition  
20       containing toner particles which do not exhibit a high agglomerating force and are excellent in dispersion capability during storage and development of the composition, and which exhibit an increased agglom-  
25       erating force in the transferring step so as to suppress collapsing and flow of the picture image, leading to an improved picture image. The present invention is also intended to provide a method of

manufacturing the particular liquid toner composition.

Let us describe some Examples of the present invention. The expressions "parts" and "%" in the following description represent "parts by weight" and  
5 "% by weight", respectively.

Example 1

A dispersion of inorganic fine particles was prepared in the first step. Specifically, 900g of C-11 (trade name of hydrated titanium oxide manufactured by  
10 Ishihara Sangyo Kaisha Ltd.) was dispersed in 3,000g of a mixed solvent consisting of 48% of Isopar L (trade name of a carrier liquid produced by Exxon Inc.), 32% of toluene manufactured by Katayama Chemical Co., Ltd. and 20% of ethanol manufactured by Katayama Chemical  
15 Co., Ltd. using a dispersing apparatus "Dynomil KDL-Pilot type" having 1.4 liters of a pulverizing chamber, which is sold by Shinmaru Enterprises Inc.

Then, put in a container equipped with a stirrer, a thermometer and a reflux condenser were 43g of the  
20 resultant dispersion of the inorganic fine particles, 3750g of the mixed solvent noted above, 50g of "Dumiran C-2280 (trade name of a partially saponified ethylene-vinyl acetate copolymer manufactured by Takeda Yakuhin Inc.), and 10g of "C.I. Pigment Blue" (trade name of  
25 phthalocyanine blue manufactured by Dainichi Seika Kogyo K.K.), which was subjected in advance to a dispersion treatment within a mixed solvent using

"Dynomil" noted above. The resultant mixture was kept stirred for 30 minutes at 70°C to permit Dumiran C-2280 to be dissolved completely, followed by cooling to room temperature so as to precipitate toner particles.

5 Further, the mixed solvent of the toner particle dispersion was replaced by Isopar L, followed by adding zirconium naphthenate as an antistat so as to charge the toner particles positive.

10 Table 1 shows the properties of the resultant liquid toner composition and the result of evaluation of the picture image quality. The toner particle diameter given in Table 1 denotes a volume-based median diameter measured by a laser diffraction/scattering type particle size distribution meter LA-700  
15 manufactured by Horiba Seisaku-sho Ltd. The zeta potential in Table 1 was measured by using LEZA-600 (trade name of a laser zeta static charge gauge manufactured by Otsuka Denshi K.K. Further, the ER property was evaluated by a method shown in Figure  
20 using an Ostwald viscometer 1. As shown in Figure, an electrode 2 (copper plate) was connected inside the Ostwald viscometer 1. A liquid toner composition 3 having a toner concentration of 10% was housed in the Ostwald viscometer 1. Further, a bare copper wire 4  
25 having a diameter of 0.2 mm was arranged within the Ostwald viscometer 1 and connected to a high voltage power source 5.

For evaluating the picture image quality, the formed image was printed on a coated paper sheet by using "Mitsubishi Printing System", and the resultant printing was visually evaluated. The image density was  
5 measured by using a Mackbeth densitometer.

Table 1

	Toner particle diameter ( $\mu\text{m}$ )	Zeta potential (mV)	Kinematic viscosity		Print density D	Gradation reproduction (visual evaluation)	Overall evaluation of picture image (visual evaluation)
			0 kV	2 kV			
Example 1	2.9	+86	17.8	27.9	1.4	Good	Good
Example 2	2.8	+77	13.9	22.5	1.4	Excellent	Excellent
Example 3	2.4	+85	12.5	21.8	1.4	Excellent	Excellent
Comparative example 1	2.6	+84	10.4	10.3	1.4	Fair	Fair
Comparative example 2	2.5	+68	11.5	11.5	1.3	Poor	Poor

The kinematic viscosity (cSt) in Table 1 was measured by an Ostwald viscometer. The values in the left column denote those obtained under voltage application of 0 kV, with the values in the right column representing those under voltage application of 2 kV.

As apparent from Table 1, a good picture image quality was obtained in Example 1.

#### Example 2

5 A toner, which was charged positive as in Example 1, was prepared substantially as in Example 1, except that a fine particle dispersion was prepared by using R972 (trade name of silica fine particles having the surface made hydrophobic, which are manufactured by Nippon Aerozyl Inc.) in place of C-11, i.e., hydrated  
10 titanium oxide used in Example 1.

The properties of the resultant liquid toner composition and the result of evaluation of the picture image quality are also shown in Table 1. As apparent from Table 1, the picture image quality for Example 2  
15 was better than that for Example 1.

#### Comparative Example 1

A liquid toner composition was prepared as in Example 1, except that a dispersion of the inorganic fine particles was not used for preparing the  
20 composition. Table 1 also shows the properties of the resultant liquid toner composition and the result of evaluation of the picture image quality. As apparent from Table 1, the picture image quality for Comparative Example 1 was inferior to that for any of Examples 1  
25 and 2.

#### Example 3

Put in a container equipped with a stirrer,

a thermometer and a reflux condenser were 3,750g of a mixed solvent, 50g of Dumiran C-2280, i.e., a partially saponified ethylene-vinyl acetate copolymer referred to previously, and 10g of a 57 : 1 mixture of brilliant carmine 6B and C.I. Pigment, said mixture being manufactured by Dai-Nichi Seika Kogyo Inc. and subjected in advance to a dispersion mixing in a solvent by using "Dynomil" referred to previously. The mixed solvent noted above consisted of 48% of Isopar L, 32% of toluene, and 20% of ethanol. The resultant mixture was kept stirred for 30 minutes at 70°C. After Dumiran C-2280 was completely dissolved, 43g of the inorganic fine particle dispersion prepared as in Example 1 was added to the resultant solution, followed by cooling the mixture to room temperature so as to allow the toner particles to be precipitated. The mixed solvent of the toner particle dispersion was replaced by Isopar L, and zirconium octylate was added as a charging agent to the dispersion so as to charge the toner particles positive. Table 1 also shows the properties of the resultant liquid toner composition and the result of evaluation of the picture image quality. As apparent from Table 1, the picture image quality for Example 3 was found to be excellent as in Example 2.

#### Comparative Example 2

A liquid toner composition was prepared as in

Example 3, except that the mixed solvent of the inorganic fine particle dispersion, which was added before precipitation of the toner particles, was replaced by Isopar L, followed by adding a charging agent. Table 1 also shows the properties of the resultant liquid toner composition and the result of evaluation of the picture image quality. As apparent from Table 1, it was impossible to obtain a satisfactory picture image quality in Comparative Example 2.

As described above, the liquid toner composition of the present invention can be used quite satisfactorily in an picture image output machine of an electrophotographic system. Specifically, the toner particles in the composition are dispersed sufficiently when the composition is used for developing an electrostatic image formed on a photosensitive body surface, leading to an excellent quality of the image developed on the photosensitive body. On the other hand, when the image developed on the photosensitive body is transferred onto a supporting sheet, the viscosity of the toner layer in the picture image portion is rapidly increased by the ER effect. It follows that the collapse of the picture image and flow of the toner particles in the transfer step can be suppressed, leading to output of a high quality picture image.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore,



the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalent.

5

### CLAIMS

1. A liquid toner composition prepared by dispersing toner particles consisting essentially of a colorant and a resin in a carrier liquid, the resultant  
5 composition forming an electrorheological fluid.

2. The liquid toner composition according to claim 1, wherein toner particles consisting essentially of a colorant and a resin are dispersed in a carrier liquid, and inorganic fine particles are attached to or  
10 impregnated in at least the surface region of the toner particle.

3. The liquid toner composition according to claim 2, wherein said inorganic fine particles are made of silica or silica which is made hydrophobic in  
15 advance.

4. The liquid toner composition according to claim 2, wherein said inorganic fine particles are made of titanium oxide or titanium hydroxide.

5. The liquid toner composition according to any  
20 one of claims 1 to 4, wherein the surface of said inorganic fine particle is treated in advance with an organic material or a hydroxide.

6. The liquid toner composition according to claim 1, wherein said carrier liquid is selected from  
25 the group consisting of linear or branched aliphatic hydrocarbons, alicyclic hydrocarbons and halogenated derivatives thereof, and silicone oils.

7. The liquid toner composition according to claim 1, wherein said colorant consists of a pigment used for preparation of an ink composition or a toner composition.

5           8. The liquid toner composition according to claim 1, wherein said resin consists of an olefin resin having a carboxyl group or an ester bond.

          9. The liquid toner composition according to claim 1, further comprising at least one of an antistat  
10          and a dispersant.

          10. The liquid toner composition according to claim 9, wherein said dispersant consists of a surfactant having ethylene oxide added thereto as a hydrophilic group.

15           11. The liquid toner composition according to claim 9, wherein the amount of said antistat is 0.5 to 50% by weight based on the solid components of the liquid toner composition.

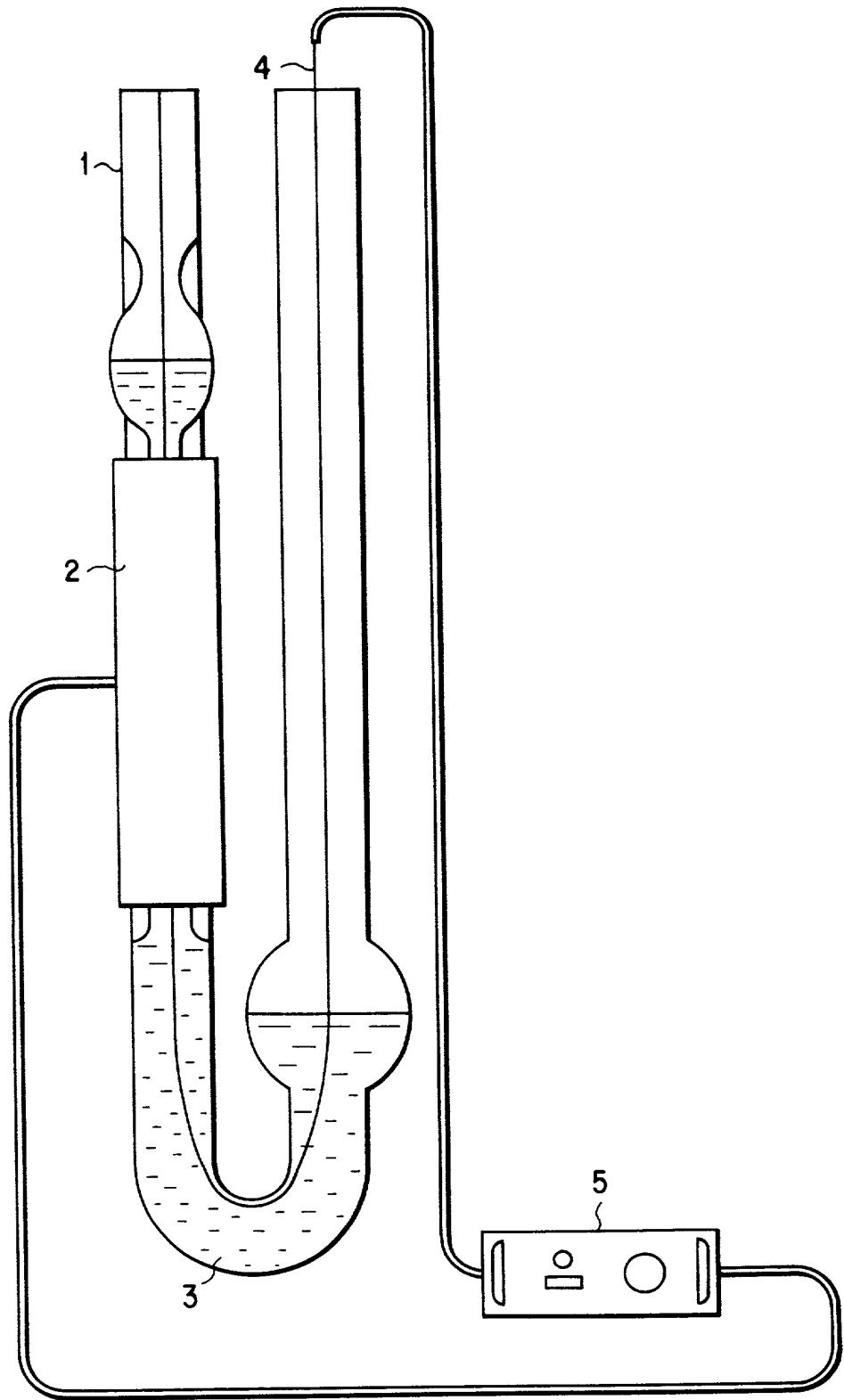
          12. The liquid toner composition according to  
20          claim 9, wherein the amount of said dispersant is 0.5 to 80% by weight based on the solid components of the liquid toner composition.

          13. A method of manufacturing a liquid toner composition, comprising the step of heating, dissolving,  
25          mixing and dispersing a thermoplastic resin in a solvent having a high temperature dependency in its capability of dissolving said thermoplastic resin and

having its solubility parameter adjusted for controlling the size of toner particles, followed by cooling to permit the toner particles to be precipitated, wherein inorganic fine particles are added by at  
5 latest the stage immediately before initiation of the toner particle precipitation.

ABSTRACT OF THE DISCLOSURE

Disclosed is a liquid toner composition prepared by dispersing toner particles consisting essentially of a colorant and a resin in a carrier liquid, the  
5 resultant composition forming an electrorheological fluid.



## DECLARATION FOR PATENT APPLICATION

97S0453-1

As a below named inventor, I declare:

that I verily believe myself to be the original, first and sole (if only one individual inventor is listed below) or an original, first and joint inventor (if more than one individual inventor is listed below) of the invention in

## LIQUID TONER COMPOSITION AND METHOD OF MANUFACTURING THE SAME

the specification of which is attached hereto unless the following box is checked.

☐ was filed on \_\_\_\_\_ as United States Application  
or PCT International Application No. \_\_\_\_\_, and  
was amended on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information of which is material to patentability as defined in 37 CFR 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365 (b) of any foreign application(s) for patent or inventor's certificate, or 35 U.S.C. 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

<u>Country</u>	<u>Category</u>	<u>Application No.</u>	<u>Filing Date</u>	<u>Priority Claim</u>
Japan	Patent	8-215765	August 15, 1996	Yes

And I hereby appoint John P. White (Reg. No. 28,678), Thomas F. Moran (Reg. No. 16,579), Norman H. Zivin (Reg. No. 25,385), Ivan S. Kavrukov (Reg. No. 25,161), Christopher C. Dunham (Reg. No. 22,031), Thomas G. Carulli (Reg. No. 30,616), Robert D. Katz (Reg. No. 30,141), Peter J. Phillips (Reg. No. 29,691), Richard S. Milner (Reg. No. 33,970), Matthew J. Golden (Reg. No. 35,161), Albert Wai-Kit Chan (Reg. No. 36,479) and Lewis Kreisler (Reg. No. 38,522), each of whose address is 1185 Avenue of the Americas, New York, N.Y. 10036, or any one of them, my attorneys with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, and request that correspondence be directed to Cooper & Dunham LLP, 1185 Avenue of the Americas, New York, N.Y., 10036

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

## DECLARATION FOR PATENT APPLICATION

I declare further that my citizenship, residence and post office address are as stated below next to my name:

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